THE VELOCITY OF TRANSFORMATION OF THE OXIMES AND THEIR DERIVATIVES

by

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I N D E X

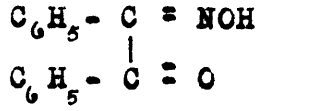
INTRODUCTION.

In 1883 Goldschmidt and Meyer (Ber., 16, 2176) discovered a second dioxime of benzil, the existence of which they could not explain by any current theory. At this time the possiblity of a three-dimensional nitrogen atom had not been discussed. Accordingly a little later Auwers and Meyer ( ) devoted considerable time to the investigation of these dioximes recognising that if their existence was not a case of mere physical isomerism (allotropism) it was apparently in direct contradiction to van't Hoff's second hypothesis of free rotation about a single bond (that two carbon atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is possible for only those substances of the type $\gtrless C - C \lessgtr$ which cannot be converted into the same form by rotation about the common axis). Auwers and Meyer (Ber, 22, 534.) found it also possible to prepare two isomeric benzilmonoximes and by the action of hydroxylamine on one of these monoximes they were able to prepare a third benzildioxime. (Ber, 22, 405.)

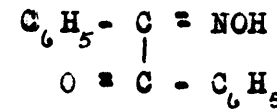
To explain this series of oximes they thought it necessary to assume that van't Hoff's second hypothesis did not always hold: that the free rotation about their common axis of two singly bound carbon atoms might in certain cases be arrested in certain definite positions, thus producing different space arrangements/

arrang ements of the molecule. On this hypothesis the oximes of benzil were formulated thus -

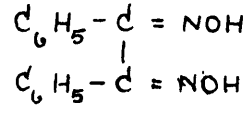
Monoximes



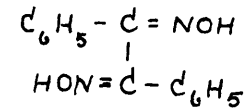
and



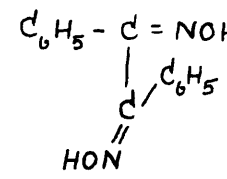
Dioximes



I.



II



(In iii the upper and lower parts of the molecule are in two planes at right angles to one another).

The objection is that there seems to be no reason why the number of the oximes should be limited, of monoximes to two and of dioximes to three. The theory was finally disposed of by the discovery of the existence of isomeric unsymmetrical ketoximes of the substituted benzophenoneoxime type containing no $\gtrless C - C \lesseqgtr$ linkage.

About this time Beckmann (Ber, 20, 2466,) announced the discovery of a second benzaldoxime. He found that it was possible to prepare a benzyl derivative from each oxime: and further that the derivative of the ordinary oxime contained the -O Benzyl group while the derivative of the iso-oxime contained the -N Benzyl group. He therefore, not unreasonably, attributed the isomerism to a difference in structure/

structure of the oximido group and assigned the formulae -

α- or ordinary oxime $C_6H_5CH=NOH$

α- or ordinary oxime

C_6H_5CH-NH (O)

β- or iso-oxime

(Ber., 22, 429, 514, 1531.)

Goldschmidt (Ber., 23, 2163.) carried out experiments on the alkylation of the oximes and shewed conclusively that both isomers can form alkyl derivatives of the type XCH=NOR.

In 1890 appeared the first of Hantzsch and Werner's classic papers (Ber., 23, 11). They pointed out that till then geometrical considerations regarding the arrangement of the atoms in molecules had been confined for the most part to the carbon atoms. It appeared to them that an application of the same principles to the nitrogen atom might lead to an explanation of these cases of isomerism without making any modification of van't Hoff's second hypothesis. Their argument was briefly as follows. If van't Hoff's second hypothesis (that "the valencies of the carbon atom are equally distributed in space and correspond to the corners of a regular tetrahedron inscribed in a sphere") be accepted it is evident that in the cyanogen compounds and in those carbon--nitrogen ring compounds in which all the valencies of the nitrogen atom are combined with carbon (e.g. pyridine and thiazole) these valencies cannot lie in the same plane as the nitrogen atom. It seems reasonable to suppose that there must be/

be some bending of the nitrogen bonds to meet those of the carbon atom in such compounds. From these considerations they deduced the hypothesis that in certain compounds the valencies of the nitrogen atom are directed towards the corners of a tetrahedron, not necessarily regular, the nitrogen atom itself occupying the fourth corner.

Hantzsch and Werner's views on the oximes may be summarised thus:

1. The oximes $\rangle C = NOH$ behave as tautomeric compounds and yield two different series of alkyl derivatives having the structural formulae

$\rangle C = NOR$ and $\rangle C \begin{matrix} - \\ O \end{matrix} \diagdown\!\diagup NR$

which may distinguished as "oxygen ethers" and "nitrogen ethers".

2. Certain asymmetrical oximes exist in two stereochemically isomeric forms which may be represented thus:

$X - \underset{\underset{HO-N}{\|}}{C} - Y$ and $X - \underset{\underset{N-OH}{\|}}{C} - Y$

3. Each of these isomerides can yield two structurally isomeric alkyl derivatives and therefore an asymmetrical oxime of the type $\begin{matrix} X \\ Y \end{matrix}\rangle C = NOH$ should yield four alkyl ethers

$X - \underset{\underset{RO-N}{\|}}{C} - Y$ structural isomers $X - \underset{\underset{R.N}{|}\rangle O}{C} - Y$

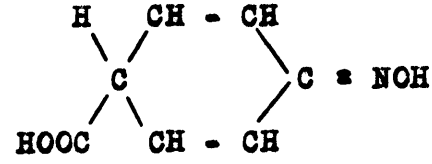
stereoisomers stereoisomers

$X - \underset{\underset{N-OR}{\|}}{C} - Y$ structural isomers $X - \underset{\underset{N.R}{|}\rangle O}{C} - Y$

Although/

Although two isomeric O-ethers had been obtained from several aldoximes and ketoximes, until 1918 all attempts to prepare a second N-ether had been unsuccessful; several alleged second N-ethers were subsequently proved to be hydrates. Semper and Lichtenstadt (Ber., 1918, 51, 928) obtained two N-ethers of p-tolylketoxime but although they also isolated two O-ethers one was an uncrystallisable oil and therefore of doubtful purity. In 1924, however, two complete series of two crystalline N-ethers and two crystalline O-ethers were described. The first series was obtained by Plowman and Whitely (T., 1924, 125, 587). from the mesoxmono-p-tolylamide oximes $NH_2CO.C(:NOH).CONHC_7H_7$ and the second by Brady and Mehta (T., 1924, 125, 2297) from the oximes of p-nitrobenzophenone. So far only one N-ether has been obtained from any aldoxime.

Hantzsch's theory receives strong support from the work of Mills and Bain (T., 1910, 97, 1870.) who succeeded in resolving the oxime of cyclohexanone carboxylic acid into two optically active forms



This would be possible only if the molecule were rendered asymmetric by the oxime hydroxyl occupying a different plane from/

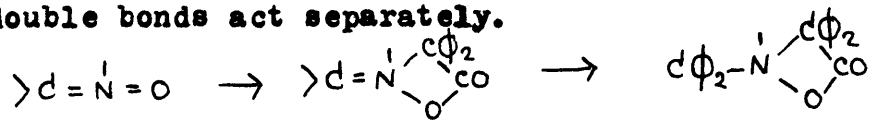
from that of the hydrogen and carboxyl.

The Hantzsch-Werner theory provided a simple explanation of known facts and in spite of adverse criticism has successfully held its ground, though it is now recognised that to explain some reactions satisfactorily a structural addition to the theory is necessary, e.g. to explain the ethers of the oximes

1. R - C - R' (Alk.N = O) ("syn" and "anti")

11. R - C - R' (NOAlk.) ("syn" and "anti")

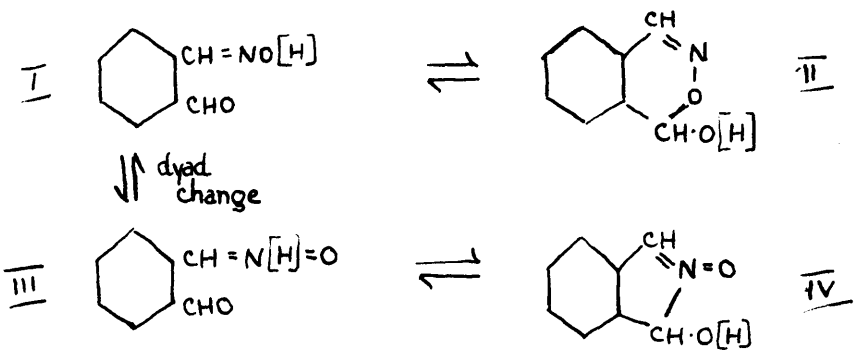
There is a considerable amount of evidence for the nitrone formula (1.) for the nitrogen ethers, (e.g. towards diphenylketen, an almost universal reagent for double linkings, both the double bonds act separately.



Staudinger and Miescher Helv.Chim. Acta, 1919, 2, 554.) and Griffiths and Ingold (T., 1925, 127, 1698.) have adduced evidence of dyad migration in oximes

$$(H)\,N = O \rightleftharpoons N.O(H)$$

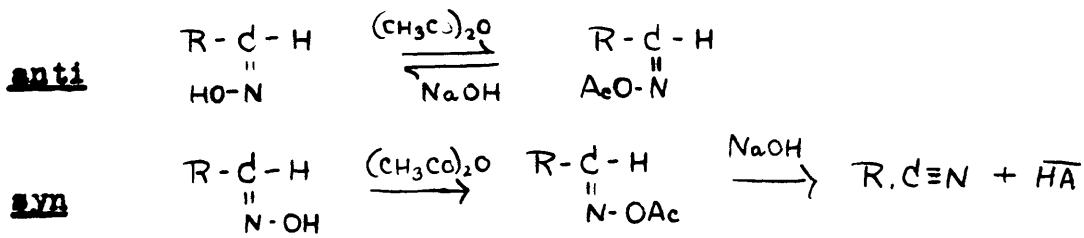
in a series of striking experiments on phthalaldehyde oxime.



The/

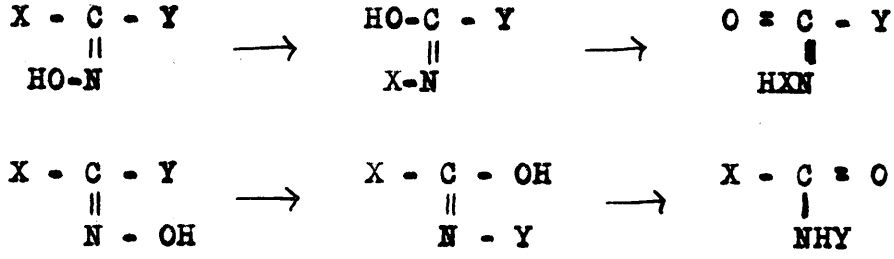
The chemical changes to be expected from the simple dyad change I. to III. become magnified by the production through ring closure of the more distinctive structures II. and IV.

In the case of ethylene isomers it was formerly taken for granted that in intramolecular reactions changes will occur most easily when the reacting atoms are situated near one another in the molecule and the methods suggested by Hantzsch (Ber., 1891, 24, 13.) and accepted for many years for the determination of the configurations of the carbon--nitrogen isomers are based on the same assumption. The aldoximes are treated below 30° with acetic anhydride: the resulting acetyl derivatives are treated with dilute caustic soda solution when it is found that one is hydrolysed with regeneration of the original oxime, while the other, by elimination of acetic acid, gives the nitrile. On the assumption that cis-elimination takes place Hantzsch gave the names anti and syn oximes respectively to these

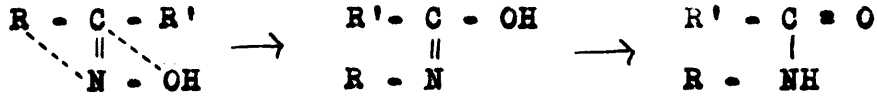


The assumption has the virtue of simplicity but in view of subsequent discoveries of cases of trans-addition and trans--elimination in ethylenic compounds such apparently axiomatic assumptions/

assumptions must be made guardedly (c.f.the work of Michael J.pr.Ch.,1892, 46, 210, 230; 1895, 52, 307, 352.). The ketoximes are differentiated by the products of the Beckmann Rearrangement which has usually been formulated thus (adopting the arbitrary convention of cis rather than trans interchange of radicles),

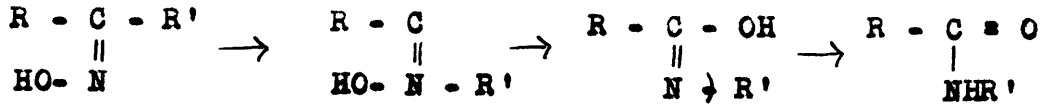


This interpretation of the Beckmann Rearrangement has been criticised by various workers; Bucherer "Lehrbuch der Farben-:chemie" 1914 suggested that trans interchange of groups took place and suggested tne following mechanism



which has the advantage that it does not involve a rupture of the molecule as the postulate of cis interchange does, while Meisenheimer and his co-workers (Ber., 1921, 54, 3195, 3206; 1924, 57, 276, 282, 289.) have adduced experimental evidence for a reversal of the existing conception and suggest the following mechanism involving trivalent carbon and tetravalent nitrogen/

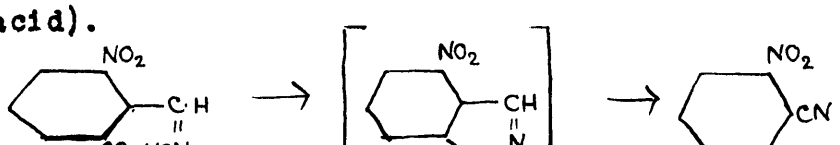
nitrogen



Reversal of the previously accepted constitutions of the isomeric aldoximes has also been proposed. Beckmann, Liesche and Correns (Ber., 1923, 56, 341.) base their arguments on Abegg's electrochemical view of the stability of oximes (Ber., 1899, 32, 291.). Abegg's statement that the α-oximes are stable to alkali and the β-oximes to acid is incorrect, since it is a well-known fact that aromatic β-aldoximes and their O-methyl ethers are rapidly converted into the correspond :ing α-compounds by the action of a small amount of acid [c.f. Luxmoore (T., 1896, 69, 179); Brady and Dunn (Ib.1923, 123, 1788.)] while they are comparatively stable when dissolved in alkali (Brady Ib.1914, 105, 2114.). Moreover if Abegg's statement were true it would afford strong evidence against the Hantzsch-Werner hypothesis since such characteristic behaviour could be due only to structural isomerism. von Auwers and Ottens (Ber., 1924, 57, 446.) arrive at similar conclusions from an examination of the optical properties of the oximes and related substances. It is doubtful, however, whether evidence based on exaltation of molecular refractivity is a real criterion where small differences of structure are concerned/

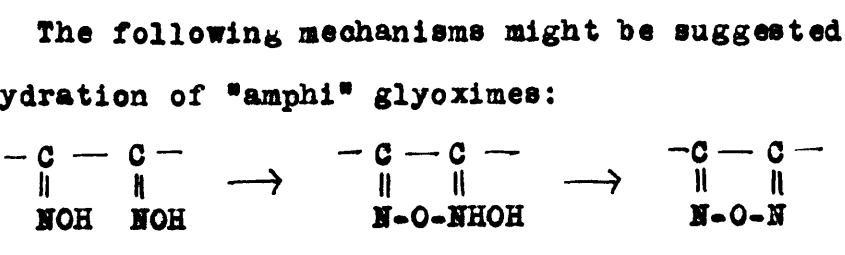
concerned, in view of the modern opinion that such "exaltation" is merely a manifestation of the existence of one or more absorption bands in the vicinity of the wave length at which the measurements are made. In this event, since obviously any arbitrary wave lenghh will bear different relationships to the absorption spectra of different substances, it would seem impossible to achieve any consistencies except in the case of compounds of the same optical "family". (C.f. inter alia Goss, Ingold and Thorpe T., 1924, 125, 1927.) Brady and Bishop (T., 1925, 127, 1357) have investigated the action of alkalis on Ortho-halogen substituted aldoximes. The benz-iso-oxazole cannot be isolated since it undergoes tautomeric change to the hydroxy-nitrile. Neither of the chlorobenzaldoximes reacts very readily (if at all), but the introduction of a nitro group renders the chlorine more reactive. Brady and Bishop have prepared the two forms of 2-chloro-5-nitrobenzaldoxime. The isomeride assigned the "anti" configuration by Hantzsch's method is found to be very stable to caustic soda solution; it does not give any ionisable chlorine when heated at 50° for four hours with N/2 caustic soda solution and is almost unchanged by boiling for four hours with N/2 caustic soda. The "syn" isomeride on the other hand gave 27% of its chlorine in ionisable form after one hour, 47% after two hours and 53% after four hours. It is/

is converted into 5-nitro-salicylo-nitrile (together with some acid).

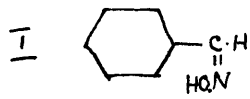


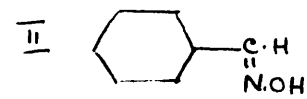
It is assumed that ring formation will take place more readily in the case where the hydroxyl group is attached to the nitrogen on the side next the halogen. If this assumption be granted then the results seem to indicate the necessity for a reversal of the usually accepted configurations. But the assumption while probably true in the majority of cases must be applied with caution since the ready dehydration of "amphi" glyoximes shews that ring closure may, in certain circumstances at least, take place by a mechanism which obviates any necessity for the eliminated residues to be originally in close proximity.

The following mechanisms might be suggested for the dehydration of "amphi" glyoximes:



Consider the evidence of dissociation constants. Ostwald (Z.ph.Ch., 1892, 9, 553) has applied to acids of the ethylene series the principle that in an acid the proximity of a so-called "acidic" group tends to increase the dissociation constant of the acid. If this holds the benzaldoximes of the anti type (I)





where the "negative" phenyl group is closer to the oximino hydroxyl than in the syn type (2) should have higher dissociation constants than the latter. Brady and Goldstein (T., 1926, 128, 1918) have found that the dissociation constants of α-aldoximes are in general considerably higher than those of the β-isomerides, thus the values found for the α- and β-benzaldoximes are:- α-benzaldoxime $2\cdot1 \times 10^{-11}$ β-benzaldoxime $0\cdot47 \times 10^{-11}$. But Brady and Chokshi (T., 1929, 946) have reaently found that the dissociation constant of benzophenoneoxime is $0\cdot50 \times 10^{-11}$. This seems to have an important bearing to which the authors make no reference. The fact that the dissociation eonstant of benzophenoneoxime (in which the hydroxyl is undoubtedly vicinal to the phenyl group) is so similar to that of β-benzaldoxime seems to suggest that in the latter compound the hydroxyl is vicinal to the phenyl group also (the implication being that Ostwald's principle does/

does not apply to the oximes) and hence that Hantzsch's configurations of the aldoximes should be reversed.

In view of the conflict of evidence regarding their constitutions Brady's suggested nomenclature of the oximes will be adopted throughout this work; the aldoximes will be referred to as α- and β- , α-aldoximes being those which on treatment with acetic anhydride at 30° yield an acetyl derivative which with caustic soda solution regenerates the oxime and β-oximes those which under the same conditions yield an acetyl derivative which with caustic soda solution yields either a nitrile or the corresponding acid.

The first measurements of the velocity of intramolecular changes of oximes and their derivatives were made by Hantzsch (Z.ph.Ch., 1894, 13, 509) who measured the velocity of transformation of acetates of β-oximes into nitriles. Later Ley (Ibid., 1895, 18, 376) repeated and extended this work and also determined the velocity of transformation of acetates of β-oximes into the corresponding derivatives of α-oximes by a most ingenious method. Determination of the velocity of transformation in solution of β-oximes into α-oximes has been attempted unsuccessfully by Dunstan and Mussel (T., 1911, 99, 571) using a viscosity method and by Brady and Goldstein (T., 1926, 128, 1921) who hoped to be able to follow the change in conductivity of the oxime solution.

The/

The method used in the present series of experiments was that developed by Patterson and McMillan (T., 1907, 91, 505; 1908, 93, 1041; Ber., 1907, 40., 2564; Trans.Roy.Phil.Soc. Glas., 1911, 42, 26). The results obtained by one of these authors in investigating the effect of inactive solvents on the rotation of optically active compounds suggested investigation of the effects of isomeric inactive solvents and that in turn extension of the investigation to solvents capable of intramolecular rearrangement. It was found possible to follow a change in rotation of the solution of a labile substance and hence to calculate the velocity of the change from the labile to the more stable form. This was an entirely new application of the polarimeter. It had, of course, been used to follow changes in active compounds (e.g.muta rotation) but this method enabled the course of a change in an optically inactive substance to be followed using an active material merely as an indicator. The method is applied as follows. A solution in ethyl tartrate containing about five per cent of the β-oxime is made up as rapidly and at as low a temperature as possible. Meanwhile the polarimeter tube has been for some time in a large thermostat on the polarimeter so that it has taken its temperature. The solution is brought to the temperature of the thermostat as rapidly as possible and then introduced into the polarimeter tube. Readings are taken at noted/

noted intervals, the rotation plotted against time and the rotation for zero time obtained by extrapolation. Then if "T" represents the interval of time measured from the time when the solution was introduced into the tube, "a" is the total change in degrees and "x" is the change in rotation in time "T" (assumed proportional to the amount of β-oxime transformed after time T) the velocity constant is given by the equation

$$K = \frac{1}{T} \log. \frac{a}{a-x}$$

the standard form of the equation for a monomolecular reaction. Patterson and McMillan (T., 1908, 93, 1045) found that the increase in the velocity of the reaction with increase in temperature in the case of piperomaloxime was in accordance with van't Hoff's equation

$$a = \frac{T_0 T_1}{T_1 - T_0} \log. \frac{k_1 T_1}{k_0 T_0}$$

The transformation of oximes in solution in dimethyl, diethyl and di-n-propyl tartrates and malates was also examined and the velocity of the reaction was found to vary from ester to ester. (Ber., 1907, 40, 2564) A most important point which emerged was that the reaction was exceedingly sensitive to slight traces of impurity in the active ester. It was also found that apparently indifferent solvents had a modifying influence on the velocity of these reactions. For example on adding to similar solutions of β-anisaldoxime in ethyl tartrate equal volumes of iso-butyl/

iso-butyl alcohol, chloroform and benzene it was found that not only was the total change of rotation which occurred in each case quite different, but the velocity of reaction was quite different also. This aspect of the reaction was very fully investigated by Patterson and Montgomerie (T., 1912, 101, 26, 2100) and will be referred to later.

AN ATTEMPT TO FOLLOW THE TRANSFORMATION OF THE ACETATES OF BENZALDOXIME.

In the present investigation it was proposed first of all to examine the behaviour of the acetates of the stereoisoneric oximes in ethyl tartrate solution in the hope that it would be possible to follow the transformation of the β-acetyl derivative to the α-acetyl derivative using the method which had been applied by Patterson and McMillan to the oximes themselves.

The ethyl tartrate used in these preliminary experiments had $\alpha^{21^\circ}_{5461}$ 100 m.m. $+9\cdot23^\circ$. It was found that a p.97·23 solution of ethyl tartrate in α-acetylbenzaldoxime had a rotation $\alpha^{21^\circ}_{5461}$ 100 m.m. $+9\cdot39^\circ$. A p.97·28 solution of ethyl tartrate in β-acetylbenzaldoxime had a rotation $\alpha^{21^\circ}_{5461}$ 100 m.m. $+9\cdot51^\circ$; after warming the solution and cooling again to room temperature the rotation was $+9\cdot37^\circ$. This gives a total change of only $0\cdot14^\circ$ which is too small for sufficiently accurate measurements to be made. Accordingly, the effect of admixture of an optically inactive solvent was tried. Benzene was chosen and a solution made up containing 18·18% ethyl tartrate and 81·82% benzene. In This solution had a rotation $\alpha^{19^\circ}_{5461}$ 100 m.m. $+0\cdot98^\circ$. A solution of β-acetylbenzaldoxime in this mixed solvent containing acetyl compound; ethyl tartrate: benzene = 6·03: 17·08: 76·88 had a rotation $\alpha^{19^\circ}_{5461}$ 100 m.m. $+1\cdot24^\circ$ while a solution of the

α-acetyl/

α -acetyl derivative containing acetyl derivative: ethyl tartrate: benzene = 5·64: 17·15: 77·19 had $\alpha^{19^\circ}_{5461}$ 100 m.m. + 1·11°
Here again the total change is too small to allow of accurate measurements being made and so this part of the investigation was discontinued for the present at least and attention turned to the transformations of the oximes themselves, especially with reference to the influence of substituents in modifying the velocity of transformation, with the view of amplifying the work started by Patterson and McMillan (Trans.Roy.Phil.Soc. Glas., loc.cit.).

THE INFLUENCE OF SUBSTITUENTS ON THE VELOCITY OF TRANSFORMATION OF OXIMES.

Patterson and McMillan's observation of the sensitivity of the active indicators to minute traces of impurity has already been referred to. In order to eliminate this source of error as completely as possible and secure comparable results over a prolonged series of experiments, a large quantity of ethyl tartrate was prepared, distilled in one lot and distributed through a number of sealed flasks in 100 g. lots, since it was thought that no material change would take place in one of these in the short time in which it would be open to the atmosphere in the course of the experiments and that the rest while sealed up would remain unaltered. This was verified by a series of check experiments with oximes whose velocity of transformation had already been determined with fair consistency. Unfortunately towards the end of the series of experiments this supply of ethyl tartrate was exhausted and a specimen prepared by a modification of Frankland and Aston's method (T., 1901, 79, 517) was used to complete the series. Two solutions of m-nitro-β- benzaldoxime in this specimen of ester were examined and gave average values for the velocity constant of 1·74 and 1·76. This gives a mean value for the velocity constant of 1·75 as compared with 1·27 in the first specimen of/

of ethyl tartrate. Accordingly the results for m-iodo- and p-methyl-benzaldoximes (the two oximes examined in this second specimen of ethyl tartrate) have been calculated on this basis to ethyl tartrate of constant 1·27 so that they can only be taken as approximate figures.

One typical experiment may be described. 0·4864 g. of dry, freshly recrystallised β-benzaldoxime was weighed out into a 15 c.c. flask, 10 c.c. ethyl tartrate pipetted in and the mixture weighed. The oxime was then brought into solution by gentle warming. The solution was rapidly cooled by immersing the flask in the thermostat and shaking. Meanwhile the polarimeter tube had been for some time in the thermostat so that it had taken its temperature. When the solution had reached the temperature of the thermostat it was introduced into the tube and the time noted. After one hour the rotation was taken and thereafter observed at intervals of forty to sixty minutes. These observed rotations were plotted against the time (in minutes) and the rotation for zero time determined by extrapolation. The end point was determined by warming the solution gently for some time then re-introducing it into the tube. This reading was compared with that obtained for a solution of α-benzaldoxime of equal concentration and found to agree within very close limits. Throughout the experiments a temperature of 25° was maintained by means of a thermo-regulator designed by Patterson (J.S.C.I., 1902, 21, 456) and all rotations were measured for the green line (5461) of the mercury/

mercury spectrum. From the data ascertained in this way the following table was constructed

T.	$\alpha^{25^\circ}_{5461}$ 100 m.m.	a - x	1000 k.
0	$+14.18^\circ$	-	-
60	13.72	2.69	2.67
135	13.23	2.20	2.66
180	12.99	1.96	2.64
215	12.85	1.82	2.55
310	12.50	1.47	2.46
370	12.30	1.27	2.45
430	12.15	1.12	2.40
∞	11.03	-	-
			Mean 2.55

The figures in the fourth column are obtained by applying the equation for a monomolecular reaction, and it will be noticed that they are fairly consistent for determinations over a considerable period of time.

It was found necessary to allow one hour to elapse after placing the solution in the tube before taking any readings since the solution on account of its viscosity took a considerable time to settle even at 25° and readings taken earlier were found unreliable.

The/

The results are collected in the following tables.

TABLE 1.

Constants determined in first specimen of ethyl tartrate.

OXIME	Approximate Concentration.	1000 k					
		Soln 1.	Soln 11	Soln 111	Soln 1V.	Soln V.	Mean
β-benzaldoxime	4	2·55	2·49	—	—	—	2·52
o-nitro-β-benzaldoxime	1·5	0·354	0·354	—	—	—	0·354
m-nitro-β-benzaldoxime	1·5	1·26	1·26	1·30	—	—	1·27
p-nitro-β-benzaldoxime	1·5	1·33	1·40	1·32	1·30	—	1·34
o-bromo-β-benzaldoxime	4	0·707	0·756	0·728	—	—	0·73
m-bromo-β-benzaldoxime	4	1·53	1·54	1·58	—	—	1·55
p-bromo-β-benzaldoxime	4	2·18	2·37	2·35	2·42	2.28	2.30
m-chloro-β-benzaldoxime	4	1·28	1·36	1·31	—	—	1·32
p-chloro-β-benzaldoxime	4	1·72	1·84	1·92	—	—	1·83
p-iodo-β-benzaldoxime	2·5	2·86	2·87	2·93	—	—	2·89
β-O-methyl-m-nitro--benzaldoxime	4	0·234	0·268	—	—	—	0·251
β-O-methyl-p-nitro--benzaldoxime	4	0·179	—	—	—	—	0·179

TABLE II.

Constants determined in second specimen of ethyl tartrate.

(prepared by Frankland and Aston's method)

	Approximate Concentration	1000 k				Mean calculated to ethyl tartrate constant 1·27
		Soln. 1.	Soln. II.	Soln. III.	Mean	
m-nitro-β-benzaldoxime	4	1·74	1·76	—	1·75	—
m-iodo-β-benzaldoxime	2½	1·79	1·71	1·77	1·76	1·27
p-methyl-β-benzaldoxime	4	2·20	2·10	2·27	2·19	1·59

TABLE III.

SUMMARY OF RESULTS.

Velocity Constants

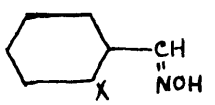
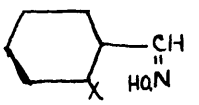
	Substituent				
Position	NO_2	Cl.	Br.	I.	CH_3
ortho	0·354	—	0·730	—	—
meta	1·27	1·32	1·55	1·27	—
para	1·34	1·83	2·30	2·89	1·59

With regard to the nitro-benzaldoximes an interesting point was noted. Patterson and McMillan (Trans.Roy.Phil.Soc. Glas., Loc.cit.) were unable to follow the transformation of p-nitro-β-benzaldoxime. In the present investigation it was observed that this oxime was only sparingly soluble in ehtyl tartrate; even a two per cent solution crystallised and it was found necessary to work with one and a half per cent solutions. It would therefore appear probable that in Patterson and McMillan's experiments the transformation had completely taken place in the preliminary heating necessary to make a five per cent solution of the oxime.

Unfortunately it has not been possible at this time to examine more than two complete series of ortho-,meta- and para-substituted benzaldoximes, the bromo- and nitro- benzaldoximes. o-iodo-β-benzaldoxime has not yet been prepared; o-chloro-β-benzaldoxime has been prepared from the α- form by Brady and McHugh (T., 1924, 125, 551) and Brady, Cosson and Roper (T., 1925, 127, 2428) but it was not found possible to prepare by their methods a sufficient quantity for the purposes of this investigation, and attempts to prepare o-methyl-β-benzaldoxime from the α-isomeride were unsuccessful (c.f.p.40.). In the two complete series which have been examined the velocity of transformation is slowest in the case of the ortho-substituted isomers/

isomers, fastest in the cases of the para-isomers and intermediate in the meta-isomers; in two other series the transformation of the meta-isomers is slower than that of the para-isomers. It seems curious that the velocity constant of p-nitro-β-benzaldoxime should have a value so close to that of m-nitro-β-benzaldoxime while in all the other cases the para-isomers are very considerably faster. It is worthy of note that the ratio of the constants of m-nitrobenzaldoxime and o-nitrobenzaldoxime agrees closely with that found by Patterson and McMillan (Trans.Roy.Phil.Soc.Glas., loc.cit.)

It is unfortunate that only two ortho-substituted benzaldoximes have been examined since the results are rather interesting. In view of the difficuly of preparing the β-modification of an ortho-substituted aromatic aldoxime from the α-isomer one might reasonably expect the transformation from β- to α-isomer to proceed fairly rapidly whereas in each of the two cases examined the average rate of transformation is very slow. This unexpected result seems only to add to the conflict of evidence regarding the structure of the oximes. Consider the ortho-substituted benzaldoximes

I  II 

One form after treatment with acetic anhydride followed by alkali/

alkali readily yields the nitrile. According to Hantzsch this should have structure (1). Yet Brady (T., 1925, 127, 1357) has shewn that this form most readily gives ring closure with a suitable ortho-substituent in the nucleus. Take, again, the evidence of dissociation constants; these were investigated by Brady and Goldstein (T., 1926, 128, 1918) who found that α-aldoximes had higher dissociation constants than β-aldoximes. Consider this result in relation to the above structural formulae. One would expect (2) to have a higher dissociation constant than (1), since, once ionisation had taken place, the steric influence of group X would tend to prevent association of the ions again. This is in agreement with Hantzsch's idea. But it is difficult to reconcile with either structure the fact that the β-modifications of ortho-substituted aldoxmines are the most difficult to prepare and yet are the most stable once they are prepared.

The effect of introduction of a nitro group into β-benzaldoxime is to impede the transformation to the α-modification. The effect of introducing halogen atoms varies considerably with the position of the substituent and the nature of the halogen. Introduction of a chlorine atom in the para position depresses the value of the velocity constant to 1·82; a bromine atom in the para position gives velocity/

velocity constant 2·30; substitution of iodine in the para-position raises the value to 2·88. This regularity is not preserved, however, in the series of meta-substituted isomers in which the values of the velocity constant are :- m-Cl 1·32, m-Br 1·55, m-I 1·27. (The last figure as has already been indicated is only approximate.) The effect of introducing a methyl group in the para-position is to depress the constant considerably.

These results are difficult to interprete. Kerr (T., 1929, p.239) has endeavoured to trace a connection between the polarity of a solvent and its influence on the velocity of a reaction. His results tend to the formulation of a hypothesis that, in general, the greater the electric moment of the solvent molecule the greater its accelerating influence on the velocity of the reaction. In the oximes we have an opportunity of studying the effect, if any, of the polarity of the transforming molecule itself. Sir J.J.Thomson (Phil.Mag., 1923, 46, 512) has analysed the polarity of disubstituted benzene derivatives. The electrical effect of replacing an atom of hydrogen by another atom or radicle may be represented, he has shewn, by the introduction of an electric doublet at the hydrogen atom, the sign of the doublet depending on the nature of the radicle; whether it is of the type of Cl, Br, I, OH, NH_2 and CH_3 (ortho para directing) or the type of NO_2, COOH, CHO and CN (meta directing). He has shewn that if the two substituents in a disubstituted benzene molecule are of the same type the electric moment will be least in the para-substituted molecule and

greatest/

greatest in the ortho-substituted one; if, on the other hand, they are of different types the moment will be greatest in the para-substituted molecule and least in the ortho-substituted one. (The electric moment governs the tendency of the molecule to "set" in an electromagnetic field and hence the specific inductive capacity is a measure of the electric moment.) Applying this to the benzaldoximes examined, we see that in the chloro-, bromo- and iodo-substituted as well as the methyl substituted oximes the electric moment should be greatest in the para substituted eximes and least in the ortho isomers; in the nitrobenzaldoximes on the other hand this order should be reversed. If, then, the polarity of the molecules bore a quantitative relationship to the velocity of transformation, (leaving the ortho-isomers out of account in view of the possibility of steric influences) it might be expected that if the m-chloro-, m-bromo- and m-iodo-β-benzaldoximes transformed more slowly than the corresponding para isomers then m-nitro-β-benzaldoxime would transform more rapidly than p-nitro-β-benzaldoxime. The experimental results do not bear this out though the values for the velocity constants of the two latter transformations are very close to one another. It may be noted that the results of Patterson and Montgomerie's work (T., 1912, 101, 2105) on the influence of optically inert solvents on the transformation of β-anisaldoxime in ethyl tartrate are directly the opposite of Kerr's. In the following table the second column of figures gives the values for the velocity constant in ethyl tartrate.

tartrate plus the solvents named, calculated to the basis of ethyl tartrate in which the velocity constant was 1·745; the first column gives the electric moment in electrostatic units multiplied by 10^{-18} (Smyth, J.A.C.S., 1924, 46, 2151; Smyth and Morgan, Ibid., 1928, 50, 1544)

Added Solvent	Electric Moment	1000 k. (Mean)
Methyl alcohol	1·78	2·07
Ethyl alcohol	1·85	1·86
n-Propyl alcohol	1·98	1·69
iso-Butyl alcohol	2·07	0·96
Allyl alcohol	1·71	1·56
Benzyl alcohol	1·74	3·14
Benzene	0·20	3·13
Toluene	0·40	2·33
o-Xylene	0·58	2.19
m-Xylene	0·46	2·34
p-Xylene	0·23	2·44
Nitrobenzene	3·90	2·94
Dimethylaniline	1·39	0·32

Kerr's results for the influence of solvents on the velocity of the reaction between allyl bromide and pyridine are given below. The figures given in brackets for the tolyl-methyl ethers are the dielectric constants.

Solvent	Electric Moment	100 k. (Mean)
Benzene	0.20	0.308
Chlorobenzene	1.56	0.924
o-Dichlorobenzene	2.25	1.566
m-Dichlorobenzene	1.48	0.866
p-Dichlorobenzene	0.00	0.799
Anisole	-	1.581
o-Tolyl-methyl-ether	(D.C. 3.57)	0.829
m-Tolyl-methyl ether	(D.C. 4.08)	1.108
p-Tolyl-methyl ether	(D.C. 4.03)	1.103
Nitrobenzene	3.90	10.15
o-Nitrotoluene	3.75	5.993
m-Nitrotoluene	4.20	4.841
p-Nitrotoluene	4.50	6.145

It will be seen that here addition of the solvent (with the exceptions of p-dichlorobenzene, nitrobenzene and m-nitrotoluene produces an acceleration of the reaction increasing with the electric moment of the solvent. The results of Patterson and Montgomerie, however, shew with a homologous series (the aliphatic alcohols) and a series of position isomers (the xylenes) precisely the reverse effect, a deceleration of the reaction with increasing electric moment. Since different reactions are being considered this does not necessarily disprove/

disprove Kerr's work, but it is of interest in shewing that if the electric moment, as seems probable, has an influence on the velocity of a reaction that influence varies from reaction to reaction; increasing electric moment does not always affect it in the same way.

As we have seen the electric moments of the oxime molecules do not seem to have any direct connection with their velocities of transformation. Consideration of the mechanism of transformation is more fruitful. In order that a molecule of a β-oxime should change into a molecule of an α-oxime the hydroxyl group must swing round from its <u>cis</u>-position to the hydrogen atom (accepting Hantzsch's configurations) to the <u>trans</u>-position, a process which necessitates rupture of the double bond between the nitrogen and carbon atoms and subsequent re-formation of the double bond. The possibility of free rotation arises once the double bond has ruptured. The rapidity of transformation would therefore appear to depend on two main factors, the ease of stabilisation of tercovalent carbon in order to allow free rotation of the parts of the molecule and the intramolecular attractions or repulsions which result in the predisposition to form the α-compound. That such a predisposition exists is shewn by the displacement of the equilibrium point so far towards a complete predominance of the α-form. The capacity of aryl groups for stabilising positively/

positively and negatively charged tercovalent carbon is discussed by Ingold (Ann.Rep.1928, pp.121, 129) and external evidence is quoted concerning their ability to stabilise neutral radicles containing tercovalent carbon e.g. the triaryl-:methyls, diaraminyls and aroxyls (ibid., pp. 150, et seq.). The same theory seems to explain fairly satisfactorily the influence of substituents on the velocity of transformation of the oximes. Ingold considers that the most satisfactory conception of the polar behaviour of the phenyl group is that its main effect is a tautomeric one of either sign ($\pm$T) and that it acts by attracting or releasing electrons according as the reaction requires it, i.e. it can absorb an electric charge of either sign produced by ionisation on an attached atom. This theory is advanced as an explanation of the well-known effect of aryl radicles in stabilising simultaneously the two ions formed by ionic dissociation of an ethane derivative as well as the neutral radicle formed in non-ionising solvents (electron octet) e.g.

$$2\ \phi_3C^{\ominus} \rightleftharpoons \phi_3C\text{-}C\phi_3 \rightleftharpoons \phi_3C^{\oplus} + \phi_3C^{\ominus}$$

The neutral radicles and the ions are represented thus on the octet theory

I $\phi_3 : C\cdot^{\ominus}$ II $\phi_3 : C^{\oplus}$ III $\phi_3 : C :^{\ominus}$

The methyl carbon in the neutral radicle (1) is affected by two factors, normally conducive to instability, which are exemplified/

exemplified also in the two ions, first the incompleteness of the octet which applies also to the positive ion (2) and second the incomplete sharing of electron which applies also to the negative ion (3). From this it is argued that a system of groups which can successfully counteract both of these factors of instability separately can also nullify them together. On this basis the process giving stability to the neutral radicle is expressed thus: "electron-release from the aryl groups partly repairs the disrupted octet and, incidentally, the disrupted duplet; the unshared pair thus partly formed is partly shared by the aryl groups". Electron-release (a tautomeric electron change) is referred to as a +T effect and the sharing of the partly formed duplet (an "inductive" effect) as a −I effect. Consider this in relation to the stabilising of tercovalent carbon and dicovalent nitrogen in a substituted benzaldoxime.

The assumptions are made that, since transfer of two electrons (with consequent development of a quinonoid structure) can only take place from the ortho- and para-positions, a somewhat similar restriction will apply to the transfer of one electron and that the substituents in the nucleus affect the carbon in preference/

preference to the nitrogen atom.

Consider first the case of para-substitution.

1. X = CH_3

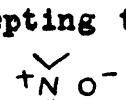
In this substituent all the valency electrons of the carbon atom are saturated so that the +T effect disappears and we have only the −I effect, the group acting as a very mild attractor of electrons.

2. X = Cl, Br, I.

With these substituents there is manifested both a +T and a −I effect. Since there is a smaller positive field in the shells of the larger atoms the +T effect will increase in the order Cl < Br < I i.e. the iodine atom will part with an electron more easily than the bromine atom and the bromine atom more easily than the chlorine; on the other hand from the same consideration the −I effect (the tendency to share the partly formed duplet) will decrease in the order Cl > Br > I.

3. X = NO_2

In this case the substituent has no disposable electrons: on the other hand accepting the formulation of the group



it appears that the positive charge on the nitrogen atom gives a strong affinity for electrons i.e. a very strong −I effect.

From these considerations one would expect stabilisation of tercovalent carbon by substituents to be in the order p-CH_3 < p-Cl < p-Br < p-I. This is borne out by the results.

A/

A modifying factor is the dicovalent nitrogen of the oximino group. Here we have an electron septet. Now nitrogen prefers a completed octet to a septet or sextet (witness formation of such compounds as sodamide and potassium carbazole) so that it would be expected to exert a strong attraction for electrons on any adjacent atom. This will mean that the influence of substituents in the aryl radicle will be modified to within considerably narrower limits.

The fact that the increase in k from Cl through Br to I is so steady leads one to conclude that the +T effect is the more important of the two and hence to deduce that with a nitro group as substituent the value of k should be considerably depressed. Moreover the values of k for a nitro group in the meta-and para-positions would be expected to be practically identical, as in fact they are.

In general the values for meta-substituents would not be expected to vary much, since the +T effect, as has already been pointed out probably disappears in this position. It is conceivable that in this position the weighting effect of the group on free rotation would play a part.

Little can be said regarding ortho-substituents on this hypothesis since it is likely that steric influences enter into play in their cases. It does seem significant, however, that the constant for o-nitro-β-benzaldoxime is so greatly depressed below that of o-bromo-β-benzaldoxime. This is quite

quite consistent with the foregoing speculations since, as has already been pointed out, the +T effect is non-existent in the nitro group.

It has long been known that the β-O-methyl ethers of the oximes are easily convertible into the corresponding α-O-methyl isomers under the influence of slight traces of hydrochloric acids and Brady has shewn that the reverse transformation from α- to β-O-methyl ethers can take place under the influence of ultra-violet light, but so far no measurements have been attempted of the velocity of either of these changes. It therefore seemed of some interest to discover whether the β- and α-O-methyl ethers transformed in ethyl tartrate in the same way as the oximes themselves and whether the effect on the optical properties of the ester was similar to that of the oximes. The behaviour in ethyl tartrate of the two forms of the O-methyl ethers of m-nitrobenzaldoxime and p-nitro-:benzaldoxime was therefore examined and it was found that the transformation of the O-methyl ether derived from the β-oxime into the O-methyl ether from the α-oxime could be followed in the same way as that of the parent oximes, though the change took place very slowly indeed. It was found that the para-substituted compound transformed rather more slowly than the meta-isomer. The N-methyl ether of m-nitrobenzaldoxime was also examined; it produced considerable exaltation of the rotation/

rotation of ethyl tartrate but the solution showed no change of rotation over a considerable period. The fact that the α- and β-O-methyl ether have respectively the same order of solvent effect as the α- and β- oximes seems a significant indication of a similar structure. Hitherto it has not been possible to assign the configurations of these ethers and the distinguishing prefixes α- and β- denoted merely the fact that these compounds were ~~derived~~ prepared from the α- and β- oximes respectively. In view of the results of the present investigation it appears that the structures are definitely the same as those of the parent oximes.

It is difficult to understand the enormously greater effect on the rotation of ethyl tartrate of β-oximes as compared with α-oximes accepting the usual formulation of these compounds as differing only in the position of a hydroxyl group. Forster and Dunn (T., 1909, 95, 425) found that diazomethane reacted with α-oximes to give O-methyl ethers while it had no action on β-oximes. Taken with Griffiths and Ingold's demonstration (T., 1925, 124, 1698) of the possibility of dyad tautomerism between the normal oxime and nitrone forms, this, at first sight, suggests the possibility of the β-oximes possessing a non-hydroxylic structure. The results of the present work with the oxime ethers seem to indicate, however, that the mechanism of transformation involves a normal oxime structure, or rather excludes an iso-oxime or nitrone structure.

Brady/

Brady and Goldstein (T.,1926, 128, 1918) have shewn that in general β-oximes have much lower dissociation constants than α-oximes; this might possibly explain their failure to form O-methyl ethers with diazomethane in view of its well-known preference for more acidic compounds.

Another point to be discussed is the catalysis of the reaction by impurities in the ethyl tartrates. Patterson and McMillan (T.,1908, 93, 1042) have shewn that purification of the ethyl tartrate by repeated fractional distillations reduced the velocity of transformation very rapidly. In the case of β-piperonaldoxime, for example, they found that in ethyl tartrate "twice distilled" the constant was 0·689, in the ester "three times distilled" 0·352 and in ester "four times distilled" 0·150. They also shewed that admixture of minute quantities of alcohol did not materially affect the constant. The ethyl tartrate used in this work has usually been prepared by the hydrochloric acid saturation method so that the most likely impurities are traces of alcohol, water, hydrochloric acid and possibly ethyl chloride. In the present work a specimen of ethyl tartrate was prepared by Frankland and Aston's continuous method in which there is no possibility of access of hydrochloric acid to the ester. Purification was carried to approximately the same degree as that of the first batch of the ester (by an equal number of distillations) and

it/

it was found that m-nitro-β-benzaldoxime transformed rather more rapidly in it than in the ester prepared by the other method: the constant found was 1·75 as compared with 1·27. It is well-known that traces of hydrochloric acid accelerate the transformation of β-oximes to α-oximes but from the above figures it would appear that there is a neglible amount present in ethyl tartrate prepared by the saturation method after it has undergone two or three fractional distillations and in view of the great difficulty of removing the last traces of moisture from ethyl tartrate it seems not unlikely that this is the catalysing influence in these transformations. This conjecture gains some support from the observation of Patterson and Montgomerie (loc. cit.) that water exerts an accelerating influence on the transformation of anisaldoxime in ethyl tartrate approximately sixty times that of ethyl alcohol, while methyl alcohol which is intermediate in character accelerates it approximately three times as much as ethyl alcohol. The relative figures are:

	1000 k
No diluent	1·745
Water	8·26
Methyl alcohol	2·07
Ethyl alcohol	1·86

EXPERIMENTS ON o-METHYLBENZALDOXIME.

In general it is found difficult, if not actually impossible, to prepare β-oximes from ortho-substituted α-benzaldoximes through the hydrochlorides. Thus no one has yet succeeded in preparing the β-modifications of o-iodo-, o-amino-, o-hydroxy-, o-methoxy- nor o-methyl-benzaldoximes in this way; o-chloro-β-benzaldoxime is obtainable only with extreme difficulty and o-bromo-β-benzaldoxime requires a special method for its preparation.

Dollfus (Ber., 1893, 25, 1912) mentions that he found it impossible to prepare the β-modification of o-methylbenzaldoxime, but it seemed worth while to reinvestigate the matter applying some of the newer methods of Brady and his co-workers.

It was decided to prepare o-methylbenzaldehyde by the Grignard reaction on ethyl orthoformate according to the scheme

$$R.MgBr + H\cdot C(OEt)_3 \longrightarrow H\text{-}C(OEt)_2R \xrightarrow{\text{hydrolysis}} R.CHO$$

where R = o-tolyl

Orthoformic ester was prepared by the method given in Organic Syntheses 5, 55. The Grignard reaction was carried out as follows. o-bromotoluene (17·1 g.), dry magnesium turnings (2·4 g.) and anhydrous etner (50 c.c.) were warmed gently together in a flask fitted with a reflux condenser. When the reaction appeared to be over orthoformic ester (14·8 g.) was added. The mixture was then heated for three hours on the water bath. It was then thoroughly shaken with ice water to decompose the additive compound, the ethereal layer containing the/

the acetal separated and the ether distilled off. The residual oil was heated under reflux for fifteen minutes with three times its volume of 5 N. hydrochloric acid to hydrolyse the acetal. The aldehyde layer was then run into concentrated sodium bisulphite solution and well shaken with it, the resulting bisulphite compound filtered off, washed with ether and dried (12 g. = 55% yield on orthoformic ester used). It was then decomposed with sodium carbonate solution, the aldehyde separated by steam distillation and oximated in the usual way using excess of caustic soda to neutralise the hydroxylamine hydrochloride and form the sodium salt of the oxime which was then decomposed by carbon dioxide. The dried oxime was recrystallised from petroleum ether. Yield 5·1 g. M.p. 47° - 48°.

A little of the α-oxime was dissolved in dry chloroform and the solution saturated at room temperature with dry hydrogen chloride. At the time hardly any precipitate formed but a considerable quantity separated out when the solution was left for some time. The solid was filtered off and washed on the filter paper with dry chloroform. After drying on porous plate in air it was found to soften at 111° and melt with decomposition at 125° - 126°. On treatment with sodium carbonate solution it gave a solid m.p. 45° - 46° - unchanged α-oxime. The chloroform mother liquor from which the hydrochloride/

hydrochloride came down was extracted with 2 N. caustic soda solution, the alkaline layer separated and saturated with carbon dioxide. A small amount of unchanged oxime was again obtained. The same result was obtained at zero and at 40°.

A solution of the α-oxime in benzene was saturated with dry hydrogen chloride at the boiling point of the solution. At this temperature no hydrochloride separated out but it was obtained on cooling. It had softening point 114°, m.p. (decomp.) 125° - 126°. On treatment with sodium carbonate solution it gave a solid m.p. 44°. The benzene mother liquor was treated in the manner previously described for the chloroform mother liquor with the same result.

The α-oxime was suspended in concentrated hydrochloric acid and hydrogen chloride passed into saturation. The hydrochloride formed seemed to be insoluble in the acid. The reaction mixture was poured into excess of sodium carbonate solution and the precipitated oxime filtered off and dried. M.p. 48°.

Dollfus' results then seemed to be confirmed.

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SUMMARY

The influence of substituents on the velocity of transformation of aromatic aldoximes has been investigated, certain regularities observed in the effect of the position of the substituents and an explanation of these suggested.

It has been found possible to follow the transformation of the oxygen-methyl ethers of m-nitro- and p-nitro-benzaldoximes polarimetrically by the method used for the oximes themselves. The rsults obtained seem to have an important bearing on the question of the configurations of these compounds.

An attempt has been made to follow the transformation of the acetyl derivatives of benzaldoxime.

Dollfus' statement that tne β-oxime of o-methyl-α-benzaldoxime cannot be prepared from the α-oxime through the hydrochloride has been reinvestigated and confirmed.

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EXPERIMENTAL DETAILS AND DATA.

m-nitrobenzaldehyde. Potassium nitrate (20g.) was dissolved in excess of concentrated sulphuric acid (50 c.c.) in a beaker. The solution was cooled below 10° and benzaldehyde (20g.) added in very small quantities at a time from a dropping funnel, the mixture being welled stirred all the time and its temperature kept below 15° . After about one quarter of the benzaldehyde had been added the mixture became pasty and remained so until the end of the preparation. After all had been added the reaction mixture was allowed to stand for an hour and then poured on ice. The solid obtained was filtered off and pressed well to remove oil. It was then transferred to a beaker and mixed thoroughly with sodium carbonate solution to remove any benzoic and nitrobenzoic acids, filtered again, washed well with water, dried on porous plate and recrystallised from carbon tetrachloride. Yield 15g. (53% of theory) m.p. 56°-58°. It is imperative that the temperature of nitration be kept well down or the yield is very greatly diminished.

The preparation of the α- and β-oximes is described subsequently.

m-nitrobenzaldehyde was the starting point for the preparation of the m-halogen-substituted benzaldehydes. Reduction with stannous chloride and hydrochloric acids without isolation of the amino-aldehyde, followed by diazotisation and Sandmeyer's reaction with cuprous chloride or bromide/

bromide gave respectively m-chlorobenzaldehyde and m-bromo-benzaldehyde (c.f. Einhorn and Gernsheim, Annalen, 284, 141.)

m-bromobenzaldehyde. m-nitrobenzaldehyde (40g.) was treated with a solution of stannous chloride (180g.) in concentrated hydrochloric acid (240 c.c.) in small quantities at a time. The reaction begins at 30°-40° but soon becomes so vigorous that external cooling must be applied. (The reaction is complete when a solution of mercuric chloride is no longer reduced, though to attain this it may be necessary to boil the reaction mixture.) On cooling the solution a red precipitate is obtained which Einhorn and Gernsheim think is probably the tin salt of the amino-aldehyde. Disregarding this precipitate the reaction mixture was diluted with about 100 c.c. water and cooled below zero in a freezing mixture. A cold aqueous solution of sodium nitrite (18·5g. in 80 c.c. water) was then run in with continual stirring and addition of crushed ice. Meantime a solution of cuprous bromide was prepared by boiling up together until the solution became colourless, copper sulphate (40g.), potassium bromide (100g.), sulphuric acid (35g.) finely cut copper foil (64g.) and 250 c.c. water. The reaction mixture containing the diazonium chloride was gradually run into the boiling cuprous bromide solution. After the reaction was complete the mixture was subjected to steam distillation when the m-bromobenzaldehyde was obtained as a heavy yellow oil. It was extracted with ether, the ether removed and the bisulphite compound made in the usual way. Decomposition of the bisulphite compound was effected with sodium carbonate

solution/

solution and the aldehyde recovered by steam distillation. It was separated from the distillate with the aid of a little ether dried over calcium chloride, the ether removed and the residual aldehyde distilled under reduced pressure. It was collected at 114°-118° under 20 m.m. pressure. Yield 27g. (55% of theory)

The preparation of the oximes is discussed subsequently.

m-chlorobenzaldehyde. m-nitrobenzaldehyde (100g.) was reduced with a solution of stannous chloride (450g.) in concentrated hydrochloric acid (600 c.c.) as described above. Without isolation, the amino-aldehyde was diazotised with 46g. sodium nitrite in aqueous solution. The diazonium solution was then added to a boiling hydrochloric acid solution of cuprous chloride made by dissolving copper carbonate (70g.) in hydrochloric acid and reducing with sulphur dioxide. Isolation of the aldehyde was effected as described above, with this exception that the aldehyde obtained from decomposition of the bisulphite compound was oximated without distillation.

p-nitrobenzaldehyde, p-chlorobenzaldehyde and p-bromobenzaldehyde were prepared by oxidation of the corresponding p-substituted toluenes either by chromyl chloride (Etard's reaction) or by chromic anhydride and sulphuric acid in presence of acetic anhydride and glacial acetic acid (c.f. Thiele and Winter, Annalen, 311, 353). o-bromobenzaldehyde was also prepared by the latter method (c.f. Brady, Cosson and Roper T., 1925, 127, 2429).

p-nitrobenzaldehyde/

p-nitrobenzaldehyde. Acetic anhydride (80g.), glacial acetic acid (80g.), concentrated sulphuric acid (30g.) and p-nitrotoluene (10g.) were mixed in the order named and the solution cooled to zero. A solution of chromic anhydride (20g.) in glacial acetic acid was then slowly added with thorough stirring, the temperature of the reaction mixture being kept within the limits 0°-10°. After all had been added the mixture was allowed to stand for about an hour and then poured on ice. The p-nitrobenzylidene diacetate was filtered off and recrystallised from spirit. Yield 13·5g. of pure product m.p. 125° (practically theoretical yield). It was found best to hydrolyse the diacetate by boiling with 30% sulphuric acid, steam distilling out the aldehyde continuously. This gave very pure p-nitrobenzaldehyde m.p.

o-bromobenzaldehyde was prepared by oxidation of o-bromotoluene by the above method using the same quantities. The o-bromobenzylidene diacetate formed gave, with one crystallisation from spirit, m.p. 84°-86°. It was hydrolysed by boiling with three times its weight of concentrated hydrochloric acid for two and a half hours. The mixture was then allowed to cool, diluted with water and extracted with ether. From the extract, on distilling off the ether, the crude aldehyde was obtained and immediately oximated. From 10g. o-bromotoluene there was obtained three to four grams of pure α- oxime.

p-bromobenzaldehyde/

p-bromobenzaldehyde. p-bromotoluene (prepared by the method given in "Organic Syntheses" Vol.5) was oxidised with chromyl chloride. p-bromotoluene (50g.) in carbon disulphide (60g.) was treated very gradually with chromyl chloride (100g.) in carbon disulphide (400g.) The reaction mixture was allowed to stand for three days and the solid which separated was filtered off and washed with carbon disulphide till the washings were colourless. The dry solid was then added gradually to about two litres ice water which was saturated with sulphur dioxide immediately all the compound had been added in order to reduce any chromic acid. A heavy oil separated and was extracted with ether. The ether was distilled off from the extract and the residue treated with concentrated sodium bisulphite solution. On decomposing the bisulphite compound formed and steam distilling the aldehyde was obtained. It crystallised from alcohol in glistening plates m.p. 57°. Yield 24g. (44% of theory).

p-chlorobenzaldehyde was prepared in the same way by treating p-chlorotoluene (15g) in carbon disulphide (60 c.c.) with chromyl chloride (25g.) in carbon disulphide (200 c.c.)

Preparation of α- aldoximes. The α-aldoximes were prepared by interaction of the substituted benzaldehyde with hydroxylamine in neutral or alkaline solution. The preparation of α-benzaldoxime (described later) is an example of preparation in neutral solution. Sodium acetate may conveniently be used instead of sodium carbonate for neutralisation of the hydroxylamine hydrochloride; this was done in the preparation of p-nitrobenzaldoxime. The alternative method consists in suspending the aldehyde in excess of 2N. caustic soda solution. (sufficient to neutralise the hydroxylamine hydrochloride and form the sodium salt of the oxime.) and adding an aqueous solution of hydroxylamine hydrochloride with constant shaking and gentle warming, if necessary, till a homogeneous solution is obtained. At this stage any impurity can be extracted with ether leaving a solution of the sodium salt of the oxime from which the free oxime is obtained by decomposition with carbon dioxide. This method of preparation was applied to o-, m-, and p-bromobenzaldoximes, m- and p-chlorobenzaldoximes and p-tolylaldoxime. The yields are good and the oximes obtained very pure.

Preparation of β-aldoximes. The methods used for the conversion of the α-oximes into the β-isomerides depended on the intermediate formation of a hydrochloride. Dunstan and Thole's method is outlined subsequently (vide β-benzaldoxime p. 43h.). More often the hydrochloride was formed by passing dry/

dry hydrogenchloride to saturation into a chloroform solution of the α-oxime when the hydrochloride was precipitated. The hydrochloride was then decomposed either with sodium carbonate solution, in which case the free β-oxime is obtained, or with excess of 2N. caustic soda solution, when a solution of the sodio-β-oxime results from which the free oxime is obtained by decomposition with carbon dioxide. The former method was applied to the three nitrobenzaldoximes and the latter to all the other oximes examined. An exceptional case is that of o-bromobenzaldoxime. When a chloroform solution of this α-oxime is saturated with hydrogenchloride no hydrochloride is precipitated. On extraction with 2N. caustic soda solution and saturation of the alkaline extract with carbon dioxide the β-oxime was obtained.

α-benzaldoxime was prepared by the following method. Hydroxylamine hydrochloride (3 mols.) was dissolved in water and a concentrated solution of sodium carbonate added till there was no further effervescence. Benzaldehyde (1 mol.) was then added and, as rapidly as possible, sufficient alcohol to gave a homogeneous solution. This solution was heated gently for some time on the water bath and then allowed to stand overnight. The small amount of sodium chloride which separated was filtered off, the filtrate concentrated by distillation and then poured into excess of cold water. The crude benzaldoxime, which was precipitated/

precipitated as an oil, was separated with a little ether, dried over anhydrous sodium sulphate and distilled twice under reduced pressure. Benzaldoxime was collected at 121°-122° under 11 m.m. pressure and gave m.p. 34°-35°.

β-benzaldoxime was prepared by the method of Dunstan and Thole (Proc. Chem. Soc., 1911, 27, 233.) The α-oxime was suspended in cold concentrated hydrochloric acid and gaseous hydrogen chloride passed in to saturation when the oxime dissolved The resulting solution was poured into excess of dilute aqueous sodium carbonate when the β-oxime was precipitated as a voluminous white solid. It was collected, dried on porous plate and recrystallised from benzene m.p. 130°.

Acetyl-α-benzaldoxime. (c.f. Hantzsch Ber., 1891, 24, 37; Luxmoore T., 1896, 69, 188.) α-benzaldoxime (1 mol.) was treated with excess of acetic anhydride (4 mols.) in the cold. When all the oxime had dissolved the mixture was poured into excess of aqueous sodium carbonate solution and well shaken up. The colourless oil which separated was extracted with ether and the extract dried over anhydrous sodium sulphate. The ether was removed under reduced pressure and on cooling the residual oil in ice it practically all crystallised. It was purified as far as possible by fractional melting and removal of the portions which melted first. Ultimately a product was obtained m.p. 12°-15°

Acetyl-β-benzaldoxime was prepared by the method of Hantzsch (loc.cit.) β-benzaldoxime (2g.) was treated with the minimum quantity of acetic anhydride (2c.c.). The oxime soon dissolved and after the solution had been left for a minute or two it was poured into ice water where it solidified almost immediately. The white crystalline derivative was removed dried on porous plate and recrystallised from warm xylene. m.p. 54°-55°

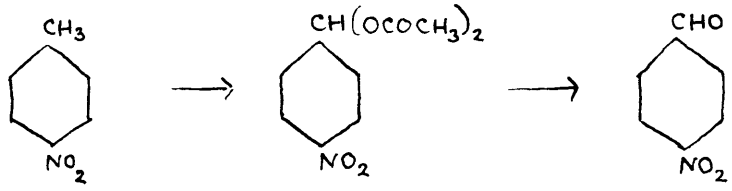
The acetyl derivatives of α- and β-benzaldoxime were prepared by the methods described by Hantzsch (Ber., 1891, 24, 34) and Luxmoore (T., 1896, 69, 188). The α-derivative was purified as far as possible by fractional melting and removal of the first portions to melt. The β-derivative, it was found, was best purified by recrystallisation from warm xylene.

m-nitro-benzaldoxime. m-nitrobenzaldehyde was prepared by nitration of benzaldehyde in the usual way. The α-oxime was prepared by treating an alcoholic solution of the aldehyde (1 mol.) with an aqueous solution of free hydroxylamine (prepared by neutralising a solution of hydroxylamine hydrochloride (3 mols.) with concentrated sodium carbonate solution). On warming up and allowing to cool the oxime crystallised out in long needles. It was recrystallised from benzene and gave m.p. 118°. The β-oxime was obtained by dissolving the α-oxime in dry chloroform and saturating the solution with dry hydrogen chloride; the precipitated hydrochloride was filtered off, dried on porous plate and treated with excess of 2 N. sodium carbonate solution. The crude β-oxime thus obtained was dried on porous plate and recrystallised from benzene. m.p.122°.

o-nitro-benzaldoxime. The specimen of α-oxime used was one remaining from the previous experiments of Patterson and McMillan. The β-oxime was prepared by the method described above/

above for m-nitro-β-benzaldoxime.

p-nitro-benzaldoxime. p-nitrobenzaldehyde was prepared by oxidation of p-nitrotoluene with chromic anhydride in presence of glacial acetic acid, acetic anhydride and concentrated sulphuric acid, and subsequent hydrolysis of the nitro-:benzylidene diacetate formed



c.f. Thiele and Winter (Annalen 311, 353). It was found best to hydrolyse the diacetate by boiling with 30% sulphuric acid steam distilling out the aldehyde continuously. The α-oxime was prepared by warming together in aqueous alcoholic solution p-nitrobenzaldehyde (1 mol.), hydroxylamine hydrochloride (3 mols.) and sodium acetate (3 mols.). On cooling the oxime crystallised out. It was crystallised from benzene giving needles m.p. 128°. The β-oxime was prepared in the same way as m-nitro-β-benzaldoxime. It was recrystallised by dissolving it in acetone at the ordinary temperature and adding water drop by drop with constant stirring and scratching. m.p. 131°.

o-bromo-benzaldoxime. o-bromobenzaldehyde was prepared by oxidation of o-bromotoluene with chromic anhydride (Brady, Cosson and Roper T., 1925, 127, 2429). The o-toluidine used for the preparation of the o-bromotoluene was first purified via the acetyl derivative. Sandmeyer's method was most unsuccessful/

unsuccessful (giving chiefly o-cresol), and finally Gatterman's method was used. The yields of o-bromotoluene were very poor - never more than 30% of theory. The α- and β-oximes were also prepared by the method of Brady, Cosson and Roper (loc.cit.).

m-bromo-benzaldoxime. m-bromobenzaldehyde was prepared from m-nitrobenzaldehyde by reduction with stannous chloride and hydrochloric acid followed by diazotisation and Sandmeyer's reaction with cuprous bromide as described by Einhorn and Gernsheim (Annalen 284, 141). The α-oxime was prepared by the same method as o-bromo- α-benzaldoxime. The β-oxime was prepared as follows; the α-oxime was dissolved in chloroform and the solution saturated with dry hydrogen chloride: the precipitated hydrochloride was filtered off, dried and treated with excess of 2 N. caustic soda solution. Carbon dioxide was then passed into the solution to saturation, the precipitated oxime filtered off, dried and recrystallised from benzene. m.p.119° - 120°.

p-bromo-benzaldoxime. p-bromobenzaldehyde was prepared from p-bromotoluene by oxidation with chromyl chloride (c.f. Hantzsch Z.ph.Ch., 13, 519). The p-bromotoluene was prepared by the method given in Organic Syntheses 5 21. The α- and β-oximes were prepared in the same way as the m-bromo-benzaldoximes.

m-chloro-benzaldoxime/

m-chloro-benzaldoxime. m-chlorobenzaldehyde and its oximes were prepared by methods analogous to those use for the preparation of m-bromobenzaldehyde and its oximes.

p-chloro-benzaldoxime. The two chloro-benzaldoximes were prepared from p-chlorotoluene by methods similar to those used in the case of the p-bromo-benzaldoximes.

The m-iodo- and p-iodo-benzaldoximes used were specimens remaining from the previous experiments of Patterson and McMillan.

p-methyl-benzaldoxime. p-methylbenzaldehyde was prepared by a Grignard reaction between p-tolyl magnesium bromide and orthoformic ester carried out precisely as described for o-methylbenzaldehyde (p.40). The two modifications of the oxime were prepared by the usual methods.

The O-methyl and N-methyl ethers of m- and p- nitro- α - and β - benxaldoximes were prepared according to the methods of Brady, Dunn and Goldstein (T., 1926, 128, 2386).

α-O-methyl-p-nitrobenzaldoxime. p-nitro-α-benzaldoxime (10g.), dry silver oxide (20g.) and methyl iodide (40 c.c.) were heated together under reflux for thirty minutes. About 50 c.c. ether was added, the mixture filtered and the ether and excess of methyl iodide removed in a current of dry air. The yellow residue was ground up with 2N. caustic soda to remove unchanged oxime and any N-ether, the mixture filtered, washed with water and dried on porous plate. Yield 10g. Recrystallisation from methyl alcohol gave the pure compound m.p. 104°.

β-O-methyl-p-nitrobenzaldoxime. p-nitro-β-benzaldoxime (5g.), dry silver oxide (10g.) and methyl iodide (35 c.c.) were heated together under reflux for forty five minutes. Ether was then added, the solution filtered and the filtrate evaporated in a current of dry air. The bright yellow solid obtained was extracted with boiling petroleum ether: from the extract on cooling there crystallised 0·9g. of the pure β-O-methyl ether m.p. 71°-72°. A bright yellow residue (m.p. 200°-203°) was left, presumably impure N-methyl ether.

N-methyl-p-nitrobenzaldoxime. A solution in chloroform of p-nitro-α-benzaldoxime (6g.) was saturated with dry hydrogen chloride, the precipitated hydrochloride filtered off, dried on porous plate and dissolved in 2N. caustic soda solution (200 c.c.) The solution was shaken with methyl sulphate (10g.) for a few minutes with cooling under the tap. The ethers formed were filtered off, washed with a little water and steam distilled.

From/

From the distillate a very small quantity of β-O-methyl ether was obtained and the contents of the flask on cooling deposited 4g. of almost pure N-methyl ether. This was collected, dried, and recrystallised from benzene. m.p. 208°.

α-O-methyl-m-nitrobenzaldoxime. m-nitro-α-benzaldoxime (10g.) was dissolved in methyl alcohol, a methyl alcoholic solution of sodium methoxide (2g. sodium) added, then methyl iodide (14g.). The solution was kept at room temperature for three days. Water was then added, the yellow precipitate collected, washed with water and steam distilled. From the distillate the ether crystallised almost pure. It was recrystallised from a misture of benzene and petroleum ether. Yield 6.6g. m.p. 63°-64°.

β-O-methyl-m-nitrobenzaldoxime & N-methyl-m-nitrobenzaldoxime. c.f. preparation of N-methyl-p-nitrobenzaldoxime. 10g. of m-nitrobenzaldoxime gave 1.4g. of the β-O-methyl ether (m.p. 73°-74°) and 8g. of the N-methyl ether (m.p. 118°-119°).

The following tables afford a comparison of the melting points of the specimens of the oximes and their derivatives examined polarimetrically with the melting points recorded in the literature.

Oxime	m.p. of specimens used.	m.p. recorded in the literature.
α-benzaldoxime	35°	35°
o-nitro-α-benzaldoxime	102°	102° (Brady and Dunn, T., 1913, , 1621)
m-nitro-α-benzaldoxime	118°	120° (Ib.) 118° (Gabriel, B., 15, 3060)
p-nitro-α-benzaldoxime	128°	129° (Brady and Dunn, loc. cit.)
o-bromo-α-benzaldoxime	101°-102°	102° (Meyer, B., 1892, 25, 2188)
m-bromo-α-benzaldoxime	71°-72°	71·5° (Einhorn and Gernsheim, A., 284, 143)
p-bromo-α-benzaldoxime	114°-115°*	110°-111° (Hantzsch, Z.ph.Ch., 13, 519)
m-chloro-α-benzaldoxime	71°	70°-71° (Erdmann and Schwechten, A., 260, 63)
p-chloro-α-benzaldoxime	108°	106°-107° (Ib.)
m-iodo - α-benzaldoxime	63°	62°-63° (Patterson, T., 69, 1009)
p-iodo - α-benzaldoxime	122°	122° (Hantzsch, loc. cit.)
α-p-tolylaldoxime	80°	79°-80° (Hantzsch, loc. cit.)

* Analysis gave Br 40·19 % (Br. $C_6H_4.CH:NOH$ requires 39·99 %).

Oxime	m.p. of specimens used.	m.p. recorded in the literature.
β-benzaldoxime	130°	130°
o-nitro- β-benzaldoxime	154°	154°
m-nitro- β-benzaldoxime	122°	123° (Forster and Dunn, T., 1909, 95, 426)
p-nitro- β-benzaldoxime	181°	182°-184°
o-bromo- β-benzaldoxime	126°	126° (Brady, Cosson and Roper, T.? 127, 2430)
m-bromo- β-benzaldoxime	119°-120°	104° (Hantzsch, Z.ph.Ch., 13, 519)
p-bromo- β-benzaldoxime	162°	157° (Kjellin and Kuylenstjerna, B., 30, 1899)
m-chloro- β-benzaldoxime	118°	115°-116° (Erdmann, Schwechten, A., 260, 60)
p-chloro- β-benzaldoxime	146°-148°	146° (Ciamician and Silber, G., 37, 1, 471)
m-iodo- β-benzaldoxime	121°	114° (Patterson and McMillan, T. Roy. Phil. Soc. Glas., 1911, 42, 31.)
p-iodo- β-benzaldoxime	159°-160°	160° (Hantzsch, loc. cit.)
β-p-tolylaldoxime	125°	108°-110° (Hantzsch, loc. cit.) 128° (Patterson and McMillan, loc. cit.)

Methyl Ethers and Acetyl Derivatives.

Derivative	m.p. of specimens used.	m.p. recorded in the literature.
α-O-methyl-m-nitrobenzaldoxime	63-64°	63-63·5° (Gabriel, B., 15, 3061)
β-O-methyl-m-nitrobenzaldoxime	73-74°	74° (Brady, Dunn and Goldstein, T., 1926, 127, 2401)
N-methyl-m-nitrobenzaldoxime	118°	118-119° (Ib.)
α-O-methyl-p-nitrobenzaldoxime	104°	105° (Forster and Dunn, T., 1909, 95, 426)
β-O-methyl-p-nitrobenzaldoxime	71-72°	70° (Brady, Dunn and Goldstein, loc. cit.)
N-methyl-p-nitrobenzaldoxime	208°	208° (Ib.)
Acetyl-α-benzaldoxime	12-15°	15° (Luxmoore, T., 1896, 69, 188)
Acetyl-β-benzaldoxime	54-55°	56° (Hantzsch, B., 1891, 24, 37)

β- benzaldoxime.

1. p = 95·97 a = 3·15°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000k.
0	+14·18°	–
60	13·72	2·67
135	13·23	2·66
180	12·99	2·64
215	12·85	2·55
310	12·50	2·46
370	12·30	2·45
430	12·15	2·40
∞	11·03	–
	Mean	2·55

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11. p = 96·14 a = 3·04°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+14·02°	–
60	13·61	2·41
120	13·23	2·51
205	12·75	2·63
315	12·35	2·59
350	12·25	2·49
405	12·10	2·46
470	11·97	2·39
∞	10·98	–
	Mean	2·49

o-nitro-β- benzaldoxime.

1. p = 98·52 a = 0·36°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+ 10·96°	–
125	10·94	0·46
180	10·93	0·48
360	10·92	0·33
1440	10·84	0·28
1620	10·82	0·30
1770	10·81	0·30
2880	10·74	0·33
∞	10·60	–
	Mean	0·354

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11. p = 98·53 a = 0·38°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+10·97°	–
60	10·96	0·48
180	10·95	0·30
360	10·93	0·31
1440	10·82	0·35
1620	10·805	0·35
∞	10·59	–
	Mean	0·354

m-nitro-β-benzaldoxime.

1. p = 98·59 a = 0·94°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·24°	–
60	11·17	1·29
120	11·11	1·24
180	11·05	1·25
250	10·99	1·24
285	10·96	1·24
360	10·90	1·25
420	10·86	1·23
480	10·80	1·31
∞	10·30	–
		Mean 1·256

11. p = 98·54 a = 1·00°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·32°	–
60	11·26	1·21
110	11·19	1·27
180	11·11	1·31
240	11·07	1·28
300	11·01	1·24
370	10·95	1·25
420	10·91	1·26
∞	10·32	–
	Mean	1.26

m-nitro-β-benzaldoxime.

111. p = 98·48 a = 1·08°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·38°	-
60	11·30	1·28
130	11·21	1·32
180	11·15	1·33
240	11·095	1·26
315	11·015	1·31
360	10·98	1·28
∞	10·30	-
	Mean	1·296

p-nitro-β-benzaldoxime.

1. p = 98·66 a = 1·23°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·21°	–
60	11·19	1·41
120	11·04	1·24
240	10·88	1·30
300	10·80	1·35
360	10·73	1·37
∞	9·98	–
	Mean	1·33

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11. p = 98·56 a = 1·38°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·33°	–
70	11·19	1·53
130	11·08	1·54
190	10·98	1·54
260	10·87	1·33
300	10·84	1·46
370	10·80	1·31
430	10·73	1·33
465	10·70	1·31
1460	10·16	1·29
∞	9·95	–
	Mean	1·40

p-nitro-β-benzaldoxime.

111. p = 98·59 a = 1·34°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·30°	–
60	11·20	1·29
120	11·10	1·34
180	11·02	1·30
226	10·96	1·36
280	10·88	1·34
340	10·81	1·34
400	10·76	1·29
∞	9·96	–
	Mean	1·32

1V. p = 98·51 a = 1·38°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·34°	–
30	11·28	1·45
120	11·12	1·48
180	11·06	1·26
240	10·99	1·22
300	10·92	1·21
360	10·84	1·25
420	10·78	1·24
∞	9·96	–
	Mean	1.30

o-bromo-β-benzaldoxime.

1. p = 96·28 a = 1·11°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·66°	–
70	11·61	0·660
120	11·56	0·787
200	11·51	0·725
265	11·46	0·751
360	11·41	0·708
420	11·39	0·664
1550	10·96	0·632
∞	10·55	–
	Mean	0·707

11. p = 96·08 a = 1·21°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·73°	–
60	11·68	0·702
120	11·62	0·794
200	11·55	0·806
290	11·49	0·762
400	11·43	0·713
∞	10·52	–
	Mean	0.756

o-bromo-β-benzaldoxime.

111. p = 96·10 a = 1·26°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·75°	–
140	11·63	0·716
220	11·56	0·743
305	11·50	0·726
400	11·45	0·680
480	11·37	0·700
540	11·32	0·773
630	11·27	0·761
∞	10·49	–
	Mean	0·728

m-bromo-β-benzaldoxime.

1. p = 96·06 a = 2·24°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·64°	–
40	12·50	1·61
70	12·41	1·55
100	12·31	1·59
130	12·23	1·55
155	12·16	1·56
295	11·82	1·54
350	11·71	1·53
400	11·64	1·48
420	11·60	1·49
450	11·58	1·42
∞	10·40	–
	Mean	1·53

m-bromo-β-benzaldoxime.

11. p = 96·10 a = 2·30°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k.
0	+12·76°	–
100	12·41	1·65
130	12·33	1·59
170	12·24	1·51
200	12·14	1·57
260	12·03	1·47
300	11·94	1·47
∞	10·46	–
	Mean	1.54

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111. p = 96·04 a = 2.29°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k.
0	+12·70°	–
80	12·42	1·63
155	12·18	1·66
180	12·11	1·65
215	12·04	1·58
260	11·96	1·50
290	11·88	1·53
320	11·81	1·54
360	11·74	1·51
∞	10·41	–
	Mean	1·58

p-bromo-β-benzaldoxime.

1. p = 95·02 a = 2·53°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·82°	–
70	12·44	2·33
180	11·98	2·24
240	11·79	2·18
300	11·58	2·25
350	11·52	2·10
370	11·49	2·02
∞	10·29	–
	Mean	2·18

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11. p = 95·02 a = 2·32°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·60°	–
60	12·32	2·15
130	12·01	2·26
190	11·73	2·47
220	11·61	2·53
280	11·48	2·35
340	11·30	2·42
400	11·16	2·42
∞	10·28	–
	Mean	2·37

p-bromo-β-benzaldoxime.

LII. p = 95.01 a = 1.89°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12.18°	-
60	11.94	2.26
120	11.76	2.10
180	11.57	2.17
210	11.46	2.28
240	11.36	2.37
350	11.12	2.23
∞	10.29	-
	Mean	2.25

IV. p = 95.99 a = 2.35°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12.56°	-
60	12.24	2.44
90	12.10	2.42
180	11.73	2.42
210	11.57	2.60
255	11.48	2.41
300	11.36	2.38
330	11.27	2.41
360	11.23	2.32
∞	10.21	-
	Mean	2.42

p-bromo-β-benzaldoxime.

V. p = 95·27 a = 2·52°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·77°	–
130	12·17	2·54
160	12·06	2·43
220	11·89	2·22
280	11·69	2·21
325	11·55	1·99
∞	10·25	–
	Mean	2·28

m-chloro-β-benzaldoxime.

1. p = 95·8 a = 2·82°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+13·14°	-
70	12·89	1·33
150	12·63	1·33
180	12·54	1·33
300	12·24	1·28
380	12·05	1·29
440	11·93	1·27
1640	10·77	1·12
∞	10·32	-
	Mean	1·28

11. p = 95·85 a = 2·70°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+13·01°	-
60	12·79	1·42
110	12·63	1·38
160	12·46	1·42
210	12·33	1·38
290	12·13	1·36
400	11·90	1·32
1440	10·77	1·23
∞	10·31	-
	Mean	1·36

m-chloro-β-benzaldoxime.

111. p = 95·73 a = 2·04°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·44°	-
60	12·28	1·36
120	12·13	1·37
165	12·05	1·28
225	11·92	1·31
295	11·78	1·32
405	11·61	1·29
475	11·51	1·28
∞	10·40	-
	Mean	1·31

p-chloro-β-benzaldoxime.

1. p = 96·27 a = 3·26°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+13·36°	-
60	13·02	1·84
120	12·76	1·69
180	12·46	1·80
240	12·27	1·70
360	11·88	1·68
420	11·70	1·70
480	11·56	1·67
600	11·30	1·67
∞	10·10	-
	Mean	1·72

11. p = 96·06 a = 2·74°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+12·88°	-
60	12·60	1·80
120	12·32	1·89
180	12·11	1·83
320	11·66	1·84
390	11·48	1·83
420	11·39	1·87
480	11·28	1·83
∞	10·14	-
	Mean	1·84

p-iodo-β-benzaldoxime.

1. p = 97·58 a = 1·25°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·42°	-
60	11·22	2·90
100	11·09	3·06
160	10·96	2·87
190	10·90	2·83
240	10·78	2·99
340	10·64	2·87
420	10·58	2·65
480	10·51	2·71
∞	10·17	-
	Mean	2·86

11. p = 97·60 a = 1·26°

T	$\alpha^{25°}_{5461}$ 100 m.m	1000 k.
0	+11·44°	-
80	11·19	2·77
120	11·06	2·99
160	10·96	3·07
210	10·88	2·80
315	10·70	2·81
370	10·63	2·78
∞	10·18	-
	Mean	2.87

p-iodo-β-benzaldoxime.

111. p = 97·58 a = 1·22°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+11·40°	-
60	11·20	2·99
130	11·03	2·78
170	10·91	3·02
200	10·86	3·07
320	10·66	2·92
360	10·60	2·96
440	10·54	2·77
∞	10·18	-
		Mean 2·93

α-O-methyl-m-nitrobenzaldoxime.

p = 96·12

$$\alpha^{25^\circ}_{5461}{}_{100\ m.m.} \quad +10·31^\circ$$

N-methyl-m-nitrobenzaldoxime.

p = 95·72

$$\alpha^{25}_{5461}{}_{100\ m.m.} \quad +11·78^\circ$$

No change in the rotation of the solution was observed over a period of twelve days.

β-O-methyl-m-nitrobenzaldoxime.

1. p = 95·81 a = 0·75°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k.
0	+11·13°	-
150	11·10	0·273
360	11·08	0·192
1980	10·85	0·236
3040	10·76	0·224
5890	10·56	0·242
6245	10·56	0·229
7305	10·52	0·244
∞	10·38	-
	Mean	0·234

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11. p = 95·80 a = 0·77°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k.
0	+11·15°	-
60	11·14	0·398
1500	10·92	0·237
1800	10·88	0·239
2940	10·77	0·231
4480	10·65	0·234
∞	10·38	-
	Mean	0·268

β-O-methyl-p-nitrobenzaldoxime.

1. p = 95·86 a = 0.85°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k.
0	+10·64°	-
60	10·63	0·196
240	10·61	0·150
360	10·59	0·168
760	10·52	0·200
1480	10·42	0·202
4320	10·18	0·180
4680	10·15	0·184
5740	10·12	0·165
6070	10·10	0·166
∞	9·79	-
	Mean	0·179

α-O-methyl-p-nitrobenzaldoxime.

Solution in ethyl tartrate p = 96·07

$$\alpha^{25^\circ}_{5461}\ 100\ \text{m.m.} = +9·76^\circ$$

m-nitro-β-benzaldoxime.

In ethyl tartrate prepared by Frankland and Aston's method.

1. p = 96·01 a = 2·48°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k.
0	+13·03°	–
60	12·78	1·77
115	12·58	1·74
150	12·46	1·74
190	12·32	1·78
290	12·07	1·69
340	11·92	1·75
430	11·74	1·71
∞	10·55	–
	Mean	1·74

11. p = 95·98 a = 2·42°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k
0	+12·96°	–
60	12·71	1·82
90	12·60	1·79
160	12·35	1·81
210	12·22	1·74
330	11·91	1·72
390	11·75	1·78
460	11·65	1·69
∞	10·54	–
	Mean	1·76

m-iodo-β-benzaldoxime.

In ethyl tartrate made by Frankland and Aston's method.

1. p = 97·57 a = 1·05°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k
0	+11·40°	-
60	11·30	1·67
120	11·20	1·76
180	11·10	1·87
310	10·95	1·81
360	10·90	1·80
420	10·84	1·82
∞	10·35	-
	Mean	1·79

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11. p = 97·59 a = 1·12°

T	$\alpha^{25°}_{5461}$ 100 m.m.	1000 k
0	+11·48°	-
60	11·37	1·72
120	11·27	1·73
180	11·19	1·66
310	11·02	1·71
360	10·96	1·73
420	10·90	1·74
∞	10·36	-
	Mean	1·71

m-iodo-β-benzaldoxime.

In ethyl tartrate prepared by Frankland and Aston's method.

111. p = 97·58 a = 0·90°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k
0	+11·25°	–
60	11·16	1·75
120	11·08	1·75
195	10·98	1·83
320	10·88	1·66
420	10·76	1·87
∞	10·35	–
	Mean	1·77

p-methyl-β-benzaldoxime.

In ethyl tartrate prepared by Frankland and Aston's method.

1. p = 95·94 a = 3·06°

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k
0	+13·90°	-
160	13·03	2·09
210	12·73	2·40
255	12·63	2·11
350	12·26	2·19
410	12·11	2·15
470	11·90	2·26
∞	10·84	-
	Mean	2·20

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11. p = 95·93 a = 3·07

T	$\alpha^{25^\circ}_{5461}$ 100 m.m.	1000 k
0	+13·90°	-
140	13·11	2·18
200	12·84	2·07
230	12·70	2·16
335	12·40	2·00
380	12·21	2·10
∞	10·83	-
	Mean	2·10

p-methyl-β-benzaldoxime.

In ethyl tartrate prepared by Frankland and Aston's method.

111. p = 95·95 a = 2·93°

T	25° α 5461 100 m.m.	1000 k
0	+13·76°	-
100	13·19	2·17
130	12·96	2·45
160	12·88	2·23
270	12·38	2·36
315	12·26	2·33
∞	10·83	-
	Mean	2·27
